

HARNESSING NON-STOICHIOMETRY AND DISORDER IN THERMOELECTRIC MATERIALS

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Thermoelectric materials require an exquisite balancing of thermal and electronic transport properties. Core to achieving such a balance in thermoelectric materials is the pursuit of non-stoichiometric compositions. Non-stoichiometry serves to control the charge carrier concentration, alter the electronic structure, control electron and phonon scattering, and produce anomalies in the phononic structure. As such, the optimized material is far removed from the original parent compound. Looking to the future, a deeper understanding of non-stoichiometry and its impact on electronic and phononic transport is critical to designing the next generation of thermoelectric materials.

To convey the importance of non-stoichiometry in thermoelectric materials, we will begin with two classic case examples that highlight how non-stoichiometry profoundly alters transport in thermoelectric materials. These include (i) the alteration of the electronic structure through resonant states in PbTe and (ii) alteration to phonon transport via ‘rattling’ modes in skutterudite compounds. With this foundation, we discuss our recent efforts to control transport in pnictide and chalcogenide compounds through a combination of first principles calculations of defect structures, combinatorial growth of alloys, and bulk synthesis. For example, Figure 1 highlights how first principles calculations can offer insight into native defect populations and their impact on electronic structure. Strategies to accelerate discovery in this high dimensional phase space and critical challenges that remain serve to conclude this discussion of thermoelectric materials.

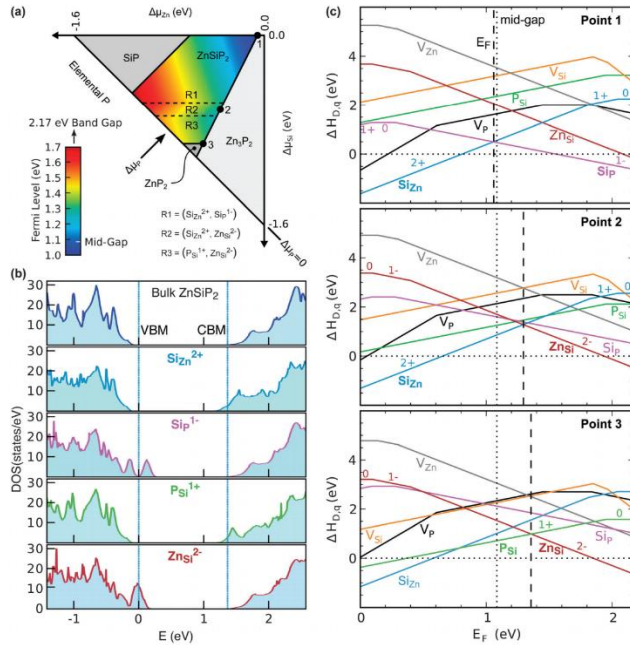


Figure 1 – (a) Calculations of the phase stability in the Zn-Si-P phase space as a function of chemical potential of the constituent species. Three distinct regimes are found for ZnSiP₂ where different dominant defect populations reign. (b) The impact of these defects on the band edge structure, and thus electronic transport, are profound and can be seen in the density of state (DOS). (c) The enthalpy of formation of specific point defects is shown for three points along the ZnSiP₂-Zn₃P₂ phase boundary. Even for a single phase material without extrinsic dopants, synthesis conditions can profoundly affect the electronic structure.